Sol-Gel Processing and Optical Nonlinearity of Gold Colloid-Doped Silica Glass

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金コロイドドーピングガラスのゾル-ゲル法による調製と光学非線形性

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Au microcrystal-doped glass films with high optical nonlinearity were prepared by the sol-gel method with dip-coating using $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ and tetraethyl orthosilicate (TEOS) as starting materials. The glass film with an Au/Si atomic ratio of 0.01 was successfully prepared. The nonlinear susceptibility $\chi^{(3)}$ of the film was 7.7×10^{-9} esu. Microcrystals with a radius of about 7 Å and of about 30 Å coexisted in the glass film. The nonlinear susceptibility of Au microcrystals itself in the film, $\chi_m^{(3)}$, was 1.0×10^{-7} esu and was two times larger than that observed in Au-doped glasses prepared by the melting method. Subsequent heat treatment of the films at 1000°C changed the absorption spectra and decreased $\chi^{(3)}$ by a factor of two. The atomic ratio of Au/Si was able to be increased to 0.04.

Key-words: Au-doped glass, Third-order optical nonlinearity, Sol-gel method, Degenerate four-wave mixing, TEM, Crystal radius, Optical absorption, Heat treatment

1. Introduction

Metal microcrystals dispersed in transparent matrix have high resonant type third-order optical nonlinearity and thus have a high potential use for all optical logic devices in the future.¹⁻⁵⁾ So, optical properties of gold microcrystals embedded in glasses, polymers or aqueous solutions were widely studied nowadays in the linear⁶⁻¹⁰⁾ and nonlinear¹⁻⁵⁾ characteristics. In particular, gold microcrystal-doped inorganic glasses¹⁻³⁾ with the microcrystal radius of 10 to 100 Å have been extensively studied because of their high optical nonlinearity, femtosecond order fast response time, convenient operating wavelength near the second harmonic of Nd: YAG laser, and thermal and photochemical stability of the matrix.

In order to use gold-doped glasses as photonic devices, glass should be made as a form of thin film waveguide. So, thin film preparation processes must be developed. Fukumi et al.^{11,12)} used the ion implantation method and obtained a gold microcrystal-

doped silica glass with the Au/Si atomic ratio of 0.22 and the third order nonlinear optical susceptibility $\chi^{(3)}$ of 1.0×10^{-7} esu. Wakabayashi et al.¹³⁾ used the r.f. sputtering method and obtained an Au-doped glass with the Au/Si atomic ratio of 0.03 and $\chi^{(3)}$ of 2.8×10^{-8} esu.

Sol-gel method using dip-coating is one of the methods for the preparation of glass films on substrate. Gold-doped silica glasses were successfully prepared with this method by the present authors¹⁴⁾ and by Kozuka and Sakka.¹⁵⁾ The former authors used sodium tetrachloroaurate ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$) as a source of Au and obtained a silica-based glass film with Au/Si atomic ratio of 0.01, and the latter authors used tetrachloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) and obtained a film with the ratio of about 0.03. However, effect of preparation condition on the microstructure and optical property of the sol-gel derived Au-doped glasses is not well understood for the present, and $\chi^{(3)}$ of these glasses has not been measured yet.

In this study, we measured the third order nonlinear susceptibility, $\chi^{(3)}$, of gold microcrystal-doped silica glass prepared by sol-gel process for the first time. Microstructure of the glass was investigated by transmitting electron microscopy, and the formation process of gold microcrystals was discussed on the bases of the distribution of crystal radius. Effects of the preparation condition and subsequent heat treatment on $\chi^{(3)}$ were discussed from the viewpoint of microstructure. Further, the effect of the concentration of NaAuCl_4 in the precursor silica solution on the glass film formation was investigated.

2. Experimental procedure

Au-doped silica glass films were prepared on silica glass plates by dip-coating method. Starting solutions were prepared from tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS), sodium tetrachloroaurate ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$), ethanol, water and HCl. Molar ratio of TEOS : NaAuCl_4 : EtOH : H_2O : HCl was 1 :

$x:6:6:0.03$, where x corresponds with the Au/Si atomic ratio and varied in the range from 0.01 to 0.06. Most of the experiments were carried out for $x=0.01$ which corresponds to 0.37 vol% of Au in the resultant Au/SiO₂ composite film. The withdrawal velocity of the silica substrate was fixed at 0.15 mm/s, resulting in a glass film with about 0.05 μm thickness after heat treatment. Heat treatment was carried out in air for 15 min at different temperatures ranging from 100° to 600°C. This dipping/heat treatment procedure was repeated several times to obtain films with sufficient thickness for optical measurements. The coated-films heat-treated once at 400°C were further heat-treated at temperatures ranging from 600° to 1000°C for 15 min to 170 h to explore the effect of post heat treatment on the optical property.

Optical absorption spectra were measured from 200 to 800 nm at room temperature. By assuming that the microcrystals are spherical and the size distribution is not so diffuse, average crystal radius of Au microcrystals was calculated from the spectra according to Eq. (1).⁷⁾

$$r = v_F / \Delta\omega_{1/2} \quad (1)$$

where r is the crystal radius, v_F the Fermi velocity of electron and 1.39×10^8 cm/s for Au, and $\Delta\omega_{1/2}$ the full width at half maximum of the absorption peak.

Crystal radius and its distribution were also measured directly by using Hitachi H-800 transmission electron microscope (TEM). For the TEM observation, Au-doped gel film was dip-coated on a platinum foil and heat-treated at 400°C for 15 min, and then the glass film was scraped out from the foil.

Third order optical nonlinear susceptibility $\chi^{(3)}$ was measured for three Au/Si=0.01 samples with different thermal history by degenerate four-wave mixing (DFWM) method at 532 nm using a Q-switched Nd: YAG laser. The duration time of the laser pulse was about 6 ns in FWHM (full width at half maximum). The $\chi^{(3)}$ of the sample was calculated by Eq. (2) with the comparison of $\chi^{(3)}/C$ of the sample with that of the standard,

$$\left| \chi^{(3)} \right| = C \cdot \frac{n^2}{L} \cdot \frac{R^{1/2}}{I_f I_b} \cdot \frac{\ln(1/T)}{T^{1/2}(1-T)} \quad (2)$$

where n , L , T , and R stand for the refractive index, thickness of the film, transmittance and the phase conjugate reflectivity of the sample, I_f and I_b are the forward and backward pump beam intensity, and $C = \lambda c / 24\lambda^3$ is a constant independent from sample where λ and c are wavelength and velocity of light. CS₂ was used as a standard sample and its $\chi^{(3)}$ was taken as 1.7×10^{-12} esu. Refractive index of the sample was assumed to be equal to that of SiO₂ glass, which is 1.461 at 532 nm, since the concentration of Au is very low. Details of the configuration of the DFWM measurement system and the method of $\chi^{(3)}$ calculation have been described elsewhere.¹⁶⁾

3. Results

Figure 1 shows the absorption spectra of gold-doped silica glass films with Au/Si=0.01 which were heat-treated at different temperatures for 15 min. Heating above 300°C induced the evolution of a peak of Au microcrystals around 545 nm in the spectrum, with the simultaneous dissipation of an absorption peak of AuCl₄⁻ anions around 310 nm. This indicates that the decomposition of AuCl₄⁻ anions and the formation of Au metal microcrystals occurred in the temperature range from 200° to 300°C. This caused the color change of the dip-coated film from colorless to purple. Except for the peak height, there is no obvious difference in absorption spectrum among the samples heat-treated from 300° to 600°C. The shape of these spectra was not affected by heating duration.

Figure 2 shows the TEM photograph of an Au-doped glass heat-treated at 400°C. Two kinds of particles with different sizes were observed. One has average radius less than 10 Å and the other has radius more than 20 Å. Both of the particles should be metallic Au, because these particles were not seen in pure silica glass prepared by similar method, and because the temperature of heat treatment was much higher than the decomposition temperature of

Fig. 1. Absorption spectra of five-times coated Au-doped glass films with the Au/Si atomic ratio of 0.01 heat-treated at different temperatures ranging from 100° to 600°C. A silica glass was used as a reference sample.

Fig. 2. TEM photograph of Au-doped glass with the Au/Si atomic ratio of 0.01 heat-treated at 400°C.

Fig. 3. Number (A) and volume (B) distributions of the Au microcrystal in the glass shown in Fig. 2.

NaAuCl₄ to Au. The number and volume distributions of the particles are shown in Figs. 3(A) and (B), respectively. More than 300 particles were accounted for obtaining the distribution. Although there is only one peak around 7 Å in the number distribution of particle radius, two peaks, around 7 Å and around 30 Å, are seen in the volume distribution of the radius. As the optical absorption coefficient is related to the volume fraction of particles,²⁾ volume distribution of the particles is important to understand the optical property of the sample.

Post heat treatment at 1000°C changed the absorption spectra of the Au-doped glass, and changed the color from purple to wine red. Figure 4 shows the absorption spectra of Au/Si=0.01 samples once heated at 400°C and then heat-treated at 1000°C for different durations up to 170 h. This post heat treatment shifted the absorption peak to the short wavelength side and increased the peak width in a short time less than 1 h. Further heating did not change the peak position but slowly made the peak width narrower, which may be caused by the increase in crystal radius.⁷⁾ The changes in position and FWHM of the peak as a function of heat treatment time is shown in Fig. 5. Apparent mean crystal radius calculated from FWHM using Eq. (1) is 40 Å for FWHM=55 nm, 34 Å for 59 nm, and 39 Å for 52 nm. As shown in

Fig. 4. Absorption spectra of ten-times coated Au-doped glass films with the Au/Si ratio of 0.01 once heat-treated at 400°C and subsequently post heat-treated at 1000°C for 1 to 170 h.

Fig. 5. Post heat treatment induced changes in absorption peak position and peak width of 400°C-heated Au-doped glass with the Au/Si ratio of 0.01 as a function of heat treatment time at 1000°C.

Fig. 6. Absorption spectra of Au-doped glass films with the Au/Si ratio of 0.01 once heat-treated at 400°C and subsequently post heat-treated at different temperatures ranging from 600° to 800°C for 1 h.

Fig. 6, similar changes in absorption spectrum were also observed after post heat treatment above 700°C, but not observed at 600°C.

Third order nonlinear susceptibility determined by DFWM method was listed in Table 1 for Au/Si=0.01 samples with different thermal history. Absorption coefficient at 450 nm, which is a linear function of the total amount of Au microcrystals as revealed for crystals with the radius larger than 5 Å,¹⁷⁾ is also listed in the table. Third order nonlinear suscep-

Table 1. Optical nonlinearity of sol-gel derived Au microcrystal-doped silica glass measured by DFWM method at 532 nm.

Preparation Condition	Absorption Peak Position (nm)	Abs. Coeff. at 450nm (μm^{-1})	$\chi^{(3)}$ (esu)
400°C	547	0.32	7.2×10^{-9}
400°C and 1000°C, 1hr	528	0.30	3.4×10^{-9}
600°C	544	0.30	7.7×10^{-9}

Fig. 7. Absorption spectra of two-times coated Au-doped glass films with different Au/Si atomic ratios which was heat-treated at 400°C. After the two-times coating and heating, the samples were wiped with tissue paper before the absorption measurement. The numerals in the figure are the Au/Si atomic ratios in the coating solutions multiplied by 100.

tibility $\chi^{(3)}$ of the sample heat-treated at 400°C was 7.2×10^{-9} esu. The $\chi^{(3)}$ of the sample heat-treated at 600°C was similar to that prepared at 400°C, being consistent with the similarity in absorption spectra of these two samples. On the other hand, the sample once heated at 400°C and then post heat-treated at 1000°C showed lower $\chi^{(3)}$ value, although the peak position in absorption spectrum was very close to the wavelength of pump and probe light in this sample.

Figure 7 shows the absorption spectra of samples with different Au contents. Au microcrystal-doped glasses with Au/Si ratio up to 0.04 were successfully prepared. Absorption spectra of the samples with Au/Si atomic ratio from 0.01 to 0.04 represent similar shape around the absorption peak with the change in intensity. The color of these films was purple in both transmission and reflection. When Au/Si ratio was increased to 0.05 or more, the obtained film became rough surfaced and was seen by naked eyes as mat gold-colored in reflection. In this case, very small gold-colored powders were formed on the surface and they were able to be wiped out easily. Similar behavior was found by Kozuka and Sakka¹⁵⁾ using $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ as a starting material. Absorption spectra shown in Fig. 7 are those after wiped, and the peak intensity of these samples was similar to that of Au/Si=0.04.

4. Discussion

Decomposition of AuCl_4^- anions and the formation of Au microcrystals occurred between 200° and 300°C in the film. This temperature is somewhat higher than the decomposition temperature of pure $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ to form metallic Au in the air. As the AuCl_4^- anion is surrounded by silica network in the gel film and thus the equilibrium of the decomposition reaction, $\text{AuCl}_4^- = \text{Au} + 3/2 \text{Cl}_2 + \text{Cl}^-$, may shift to the left hand side because of the accumulation of Cl_2 in the film due to low diffusion of Cl_2 through the gel network.

The Au atoms produced by the decomposition of

AuCl_4^- should tend to aggregate to form microcrystal. The distribution of crystal radius shows that the fraction of microcrystal with the radius of about 7Å is very high. When we assume that the structure of the microcrystal is the same as that of bulk crystal, that is fcc, and that the atomic radius of Au in the microcrystal is nearly the same as that in the bulk, then the crystal radius of 7Å corresponds to the cluster of Au_{85} (crystal radius of 6Å corresponds to Au_{54} and that of 8Å corresponds to Au_{127}). It is known that a stable Au_{55} cluster with ligands at the surface can be synthesized by chemical process,¹⁸⁾ and its structure is based on the fcc lattice like in the bulk crystal or constructed by 8 ($=2^3$) unit cells without cornered eight atoms.¹⁹⁾ Considering that the crystal radius determined by TEM has a tendency toward overestimating because of the incompleteness of focussing, therefore, the microcrystals with the radius of about 7Å in the present SiO_2 glass film may be above mentioned Au_{55} cluster, or related to it and written as $\text{Au}_{55+\alpha'}$, which may be stable as a form of bare cluster, with being coordinated by silica network, like that of a chemically synthesized ligand-covered cluster. Though Au_{13} cluster with ligands is also known to be stable as well as Au_{55} cluster,²⁰⁾ whether clusters of this type exist in this glass film or not cannot be determined because the cluster size is smaller than the TEM resolution limit.

Clusters having radius larger than 10Å may be formed by aggregation or by growth of the 7Å clusters. As the evolution of 545 nm peak and dissipation of 310 nm peak took place in a short time less than 15 min on heating the gel film at a temperature less than 600°C and longer heat treatment has no more effect, it is considered that the formation and growth of Au microcrystals occur at the gel state or during the gel to glass conversion process, and does not occur once a rigid and dense glass network is formed.

The volume fraction profile of crystal has two peaks around 30Å and around 7Å. The former fairly corresponds to the radius calculated from the FWHM of the optical absorption peak. Although the absorption by 7Å-radius microcrystals occur at similar wavelength to Au_{55} cluster which shows the absorption around 520 nm,¹⁸⁾ the very low absorption coefficient and the extremely broad peak width makes the peak undistinguishable when it is overlapped with a strong and sharp peak caused by 30Å-centered microcrystals. Thus, the crystal radius obtained from FWHM represents the average crystal radius of microcrystals involving the larger radius group in the volume distribution histogram. Eventually, the difference of average crystal radius calculated from FWHM and that observed by TEM may be originated from the too simple assumptions to derive Eq. (1).

Third order nonlinear optical susceptibility $\chi^{(3)}$ of 400°C heat-treated Au-doped glass was 7.2×10^{-9}

esu, and 7.7×10^{-9} esu for 600°C heat-treated one. The nonlinear susceptibility of Au microcrystals themselves in the film, $\chi_m^{(3)}$, can be calculated by using the following relations²⁾

$$f_1(\omega) = \frac{3 \varepsilon_d}{\varepsilon_m(\omega) + 2 \varepsilon_d} \quad (3)$$

$$\chi^{(3)} = p f_1^2 |f_1|^2 \chi_m^{(3)} \quad (4)$$

where $\varepsilon_m(\omega) = \varepsilon_m' + i\varepsilon_m''$ is the frequency dependent complex dielectric constant of Au particle, ε_d is the real part of that of the glass matrix (imaginary part is negligible at this wavelength), and p is the volume fraction of Au particles. By using the complex refractive index of bulk gold²¹⁾ for calculating $\varepsilon_m(\omega)$ and putting $\varepsilon_d = 1.461^2$, which is the square of the refractive index of silica glass at 532 nm, the $\chi_m^{(3)}$ in these two glasses was estimated as 1.0×10^{-7} esu. This value is similar to that in a glass prepared by ion implantation, that is 8×10^{-8} esu,¹¹⁾ and is also similar to the value in the sputter-derived glass calculated from the $\chi^{(3)}$ data in Ref.13). These $\chi_m^{(3)}$ values are about two times larger than that observed in Au-doped glasses prepared by melting and subsequent heat treatment.²⁾

Nonlinear susceptibility of the glass film rapidly decreased to about half when the sample was post heat-treated at 1000°C. This heat treatment also caused the shift of the absorption peak from 545 nm to 528 nm and the narrowing of the width of this peak. So the changes in nonlinear susceptibility and in absorption spectrum should be correlated. The direction of change in optical absorption with time is opposite to that expected to occur by crystal growth, then other phenomena must be considered. The major change in the absorption spectrum took place in a short time during post heat treatment, and after this the change became very slow and even opposite to the initial one, suggesting that the initial rapid change is a relaxation phenomenon of microstructure. Since the formation of Au microcrystals in the present work is very rapid, there may be a possibility to form microcrystals which have thermodynamically unstable morphology such as nonspherical clusters, and these may be reformed to thermodynamically stable microstructure by heat treatment at temperatures sufficiently high for atomic diffusion. Thus, the observed results can be explained in terms of the narrower absorption peak and higher nonlinear susceptibility of the unstable cluster above mentioned.

Optical susceptibility of the Au microcrystals themselves in the films, $\chi_m^{(3)}$, after the heat treatment at 1000°C is estimated as 6×10^{-8} esu. This value is equal to that in the glasses prepared by melting and subsequent heat treatment where the microcrystals with thermodynamically stable structure may have been formed. As both ion implantation and sputtering are high energy processes so that the obtained glasses are highly supersaturated by Au

atom, the microcrystals precipitated by subsequent heat treatment may be different from the stable structure one and have high $\chi_m^{(3)}$ values. Furthermore, the Au-supersaturated nature of the glass network may prevent the relaxation of microstructure to the low $\chi_m^{(3)}$ form. Change in absorption peak width by long time heat treatment may be due to the crystal growth.

The atomic ratio of Au/Si can be increased to 0.04 from 0.01. Further addition of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ to the coating solution was not effective to increase the Au content in the film. The absorption peak height of Au/Si=0.05 and 0.06 glasses measured after wiping the surfaces were similar to that of Au/Si=0.04 glass, implying that the excess Au is discharged from the glass film. The absorption spectrum of the glass with Au/Si=0.04 is similar to that of Au/Si=0.01 glass except for the amplitude, then, it is considered that the microstructure and the size of Au microcrystals in these glasses are the same. So, nonlinear susceptibility of about 3×10^{-8} esu would be expected by multiplying the $\chi^{(3)}$ of Au/Si=0.01 glass by the increment of the content of Au, i.e. four.

5. Conclusion

Au microcrystal-doped glass films were prepared by sol-gel method with dip-coating using $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ and TEOS as starting materials. Glass films with the Au/Si atomic ratio of 0.01 were successfully prepared by heating the gel films at a temperature ranging from 300° to 600°C. These films showed the nonlinear susceptibility $\chi^{(3)}$ of 7.7×10^{-9} esu. Microcrystals with the radius of about 7Å and of about 30Å coexist in the glass film. Subsequent heat treatment of these glass films at 1000°C shifted the absorption peak from 545 nm to 528 nm, made the width of this peak narrower, and decreased $\chi^{(3)}$ of the film by a factor of two. The nonlinear susceptibility of Au microcrystal itself, $\chi_m^{(3)}$, in the as-prepared film was 1.0×10^{-7} esu, which is nearly the same as that of glasses prepared by ion implantation or sputtering. The $\chi_m^{(3)}$ of the 1000°C-heat-treated film was about the half of this value and is the same as that observed in Au-doped glasses prepared by melting and subsequent heat treatment. The atomic ratio of Au/Si can be increased to 0.04, where $\chi^{(3)}$ of about 3×10^{-8} is expected.

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